STO - Gaussian Overlap Notes

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1. Slater Type Orbitals

Slater Type Orbitals (STO)[1] in the atomic orbital (AO) basis are used in semiempirical methods based on Neglect of Differential Diatomic Overlap (NDDO) such as AM1. STO are given by:

$$\chi_{n\ell m}(\vec{r}_A) = N_n(\xi)\, r_A^{n-1} e^{-\xi r_A} Y_{\ell m n}(\theta_A, \phi_A), \tag{1}$$

with normalization:

$$N_n(\xi) = \left(\frac{(2\xi)^{2n+1}}{(2n)!} \right)^{1/2}, \tag{2}$$

where ξ is the orbital exponent (parameter depending on the given orbital and semiempiric method such as AM1), n is the principal quantum number, $\vec{r}_A$ is the correspondent distance to the nucleus, and $Y_{\ell m n}(\theta_A, \phi_A)$ are the normalized real harmonics[2]. In these notes we'll only consider s and p types of orbitals:

$$(\ell=0, m=0) \longrightarrow |ns\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \frac{1}{\sqrt{4\pi}}, \tag{3}$$

$$(\ell=0, m=1) \longrightarrow |np_x\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}}\, \frac{x}{r}, \tag{4}$$

$$|np_y\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}}\, \frac{y}{r}, \tag{5}$$

$$|np_z\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}}\, \frac{z}{r}, \tag{6}$$

where x, y, and z are the Cartesian coordinates in the coordinate system centered in the corresponding atom.

2. Slater Type Orbitals

A primitive Cartesian Gaussian Orbital is typically writen as:

$$\phi^{(A)}_{\ell_x \ell_y \ell_z}(\vec{r}, \alpha) = N(\ell_x, \ell_y, \ell_z, \alpha)\, x^{\ell_x} y^{\ell_y} z^{\ell_z} e^{-\alpha r^2}, \tag{7}$$

where the total angular degree is $l = l_x + l_y + l_z$, α is the Gaussian exponent, and the normalization factor is given by:

$$N(l_x, l_y, l_z, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \sqrt{\frac{(8\alpha)^{l_x+l_y+l_z}\, l_x!\, l_y!\, l_z!}{(2l_x)!\,(2l_y)!\,(2l_z)!}}, \tag{8}$$

For s type GTO we get:

$$\phi_s(\vec{r}, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}, \tag{9}$$

while for p type GTO we get:

$$\phi_{p_x}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}} x e^{-\alpha r^2}, \tag{10}$$

$$\phi_{p_y}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}} y e^{-\alpha r^2}, \tag{11}$$

$$\phi_{p_z}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}} z e^{-\alpha r^2}, \tag{12}$$

3. Overlap Integrals

For deriving tractable equations for the overlap integrals we'll use the following identity (Gauss Transform):

$$e^{-\xi r} = \frac{\xi}{\sqrt{\pi}} \int_0^\infty u^{-1/2} e^{-\xi^2/4u} e^{-ur^2} du, \tag{13}$$

representing the Slater exponential as a continuos superposition of Gaussians.[3] We'll also use the Gaussian product theorem:

$$e^{-ur_A^2} e^{-\alpha r_B^2} = \exp(-\mu R^2) \exp\left[-(u+\alpha)(r-P)^2\right], \tag{14}$$

where:

$$P = \frac{uA + \alpha B}{u+\alpha}, \tag{15}$$

and:

$$\mu = \frac{u\alpha}{u+\alpha}, \tag{16}$$

3.1 s-s

Evaluating eq. (3) and eq. (9) in displaced atomic centers $\vec{A}$ and $\vec{B}$ such that $\vec{R} = \vec{A} - \vec{B}$, and $R = |\vec{R}|$, using the Gauss Transform eq. (13), swapping the integration operators, solving for the spatial integral, and using the identity:

$$r_A^{n-1} e^{-\xi r_A} = \left(-\frac{\partial}{\partial \xi}\right)^{n-1} e^{-\xi r_A}, \tag{17}$$

we get:

$$S_{ss}^{(n)}(R, \xi, \alpha) = N_n(\xi) N_{000}(\alpha) \left(-\frac{\partial}{\partial \xi}\right)^{n-1} \left[\frac{\xi}{\sqrt{\pi}} \int_0^\infty u^{-1/2} e^{-\xi^2/4u} \left(\frac{\pi^{3/2}}{(u+\alpha)^{3/2}}\right) e^{-\frac{u\alpha}{u+\alpha} R^2} du\right], \tag{18}$$

where the derivative can be recast by introducing Hermite polynomials satisfying the identity:

$$(-\partial)^n e^{-a\xi^2} = a^{n/2} H_n(\sqrt{a}\,\xi) e^{-a\xi^2}, \tag{19}$$

which yields:

$$S_{ss}^{(n)}(R, \xi, \alpha) = \left(\frac{(2\xi)^{2n+1}}{(2n)!}\right)^{1/2} \frac{1}{\sqrt{4\pi}} \left(\frac{2\alpha}{\pi}\right)^{3/4} \pi\, 2^{-(n-1)} \int_0^\infty \frac{u^{\frac{1-n}{2}}}{(u+\alpha)^{3/2}} e^{-\mu(u) R^2} e^{-\xi^2/4u} H_n\left(\frac{\xi}{2\sqrt{u}}\right) du, \tag{20}$$

3.2 s-p

Analogously, by using eqs. (10-12), we get:

$$S_{sp_k}^{(n)}(R, \xi, \alpha) = N_n(\xi) N_{100}(\alpha) \left(-\frac{\partial}{\partial \xi}\right)^{n-1} \int_0^\infty u^{-1/2} e^{-\xi^2/4u} \left(\frac{u}{u+\alpha} R_k\right) \frac{\pi^{3/2}}{(u+\alpha)^{3/2}} e^{-\frac{u\alpha}{u+\alpha} R^2} du, \tag{21}$$

where R_k is the component k of $\vec{R} = \vec{A} - \vec{B}$. Introducing again the Hermite polynomials we get:

$$S^{(n)}_{s\text{-}p_k} = \left(\frac{(2\varrho)^{2n+1}}{(2n)!}\right)^{1/2} \frac{1}{\sqrt{4\pi}} \frac{(2\alpha)^{5/4}}{\pi^{3/4}} \pi\, 2^{-(n-1)} R_k \int_0^\infty \frac{u^{\frac{3-n}{2}}}{(u+\alpha)^{5/2}} e^{-\mu(u) R^2} e^{-\varrho^2/4u} H_n\left(\frac{\varrho}{2\sqrt{u}}\right) du, \qquad (22)$$

3.3 p-s

Using now eqs. (4-6), we get:

$$S^{(n)}_{p_k\text{-}s}(R,\varrho,\alpha) = N_n(\varrho) N_{000}(\alpha) \left(-\frac{\partial}{\partial \varrho}\right)^{n-2} \Bigg[\frac{\varrho}{\sqrt{\pi}} \int_0^\infty u^{-1/2} e^{-\varrho^2/4u} \left(-\frac{\alpha}{u+\alpha} R_k\right) \frac{\pi^{3/2}}{(u+\alpha)^{3/2}} e^{-\frac{u\alpha}{u+\alpha} R^2} du, \qquad (23)$$

or introducing the Hermite polynomials:

$$S^{(n)}_{p_k\text{-}s} = -\left(\frac{(2\varrho)^{2n+1}}{(2n)!}\right)^{1/2} \sqrt{\frac{3}{4\pi}} \left(\frac{2\alpha}{\pi}\right)^{3/4} \pi\alpha\, 2^{-(n-2)} R_k \int_0^\infty \frac{u^{\frac{2-n}{2}}}{(u+\alpha)^{5/2}} e^{-\mu(u) R^2} e^{-\varrho^2/4u} H_{n-1}\left(\frac{\varrho}{2\sqrt{u}}\right) du, \qquad (24)$$

3.4 p-p

Using eqs. (4-6) and eqs. (10-12) we get:

$$S^{(n)}_{p_k\text{-}p_l}(R,\varrho,\alpha) = N_n(\varrho) N_{100}(\alpha) \left(-\frac{\partial}{\partial \varrho}\right)^{n-2} \Bigg[\frac{\varrho}{\sqrt{\pi}} \int_0^\infty u^{-1/2} e^{-\varrho^2/4u} \frac{\pi^{3/2}}{(u+\alpha)^{3/2}} e^{-\frac{u\alpha}{u+\alpha} R^2} \times$$

$$\times \left\{ \left(-\frac{\alpha}{u+\alpha} R_k\right)\left(\frac{u}{u+\alpha} R_l\right) + \frac{\delta_{kl}}{2(u+\alpha)} \right\} du, \qquad (25)$$

or introducing the Hermite polynomials:

$$S^{(n)}_{p_k\text{-}p_l} = \left(\frac{(2\varrho)^{2n+1}}{(2n)!}\right)^{1/2} \sqrt{\frac{3}{4\pi}} \frac{(2\alpha)^{5/4}}{\pi^{3/4}} \pi\, 2^{-(n-2)} \int_0^\infty \frac{u^{\frac{2-n}{2}}}{(u+\alpha)^{3/2}} e^{-\mu(u) R^2} e^{-\varrho^2/4u} H_{n-1}\left(\frac{\varrho}{2\sqrt{u}}\right) \times$$

$$\times \left[\left(-\frac{\alpha}{u+\alpha} R_k\right)\left(\frac{u}{u+\alpha} R_l\right) + \frac{\delta_{kl}}{2(u+\alpha)} \right] du, \qquad (26)$$

4. Quadrature

In order to calculate numerically the relevant integrals, let's introduce the following substitution:

$$u = \frac{\xi^2}{4t}, \tag{27}$$

$$du = -\frac{\xi^2}{4t^2}\,dt, \tag{28}$$

for which the integrals become:

$$\int_0^\infty e^{-t} G(t)\,dt, \tag{29}$$

where:

$$G(t) = N\left(\frac{\xi^2}{4}\right)^{a+1} t^{-(a+2)}\, B(t)^{-b} \exp\left[-\mu(t) R^2\right] H_m(\sqrt{t})\, A(t,R), \tag{30}$$

where:

	s-s	s-p_k	p_k-s	p_k-p_ℓ
N	$N_{no}(\xi) N_s(\alpha) \pi\, 2^{-(n-1)}$	$N_{no}(\xi) N_p(\alpha) \pi\, 2^{-(1-n)} R_k$	$-N_{STO,p}(\xi) N_s(\alpha) \pi \alpha\, 2^{-(n-2)} R_k$	$N_{STO,p}(\xi) N_p(\alpha) \pi\, 2^{-(n-2)}$
a	$-\frac{(n-1)}{2}$	$-\frac{(n-3)}{2}$	$-\frac{(n-2)}{2}$	$-\frac{(n-2)}{2}$
b	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{3}{2}$
m	n	n	$n-1$	$n-1$
$A(t,R)$	1	1	1	$\left(-\frac{\alpha}{B(t)} R_k\right)\left(\frac{u(t)}{B(t)} R_\ell\right) + \frac{\delta_{k\ell}}{2B(t)}$

where we have introduced:

$$B(t) = \alpha + \frac{\xi^2}{4t}, \tag{31}$$

Finally, the integral in eq. (29) can be calculated by means of the Gauss-Laguerre node/weights:

$$\int_0^\infty e^{-t} G(t)\,dt = \sum_{i=1}^{N} w_i\, G(t_i), \tag{32}$$

Tip: Use N=32 as a default and check against 48 and 64 for convergence when developing

References

[1] James J. P. Stewart, "Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and applications to 70 elements", J. Mol. Model. (2007) 13: 1173-1213.

[2] Miguel A. Blanco, M. Flórez, M. Bermejo, "Evolution of rotation matrices in the basis of real spherical harmonics," Journal of Molecular Structure (Theochem) 419 (1997) 19-27.

[3] André Severo Pereira Gómez, Rogelio Custodio, "Exact Gaussian Expansions of Slater Type Atomic Orbitals", Journal of Computational Chemistry, 23.10 (2007) 1007-1012.